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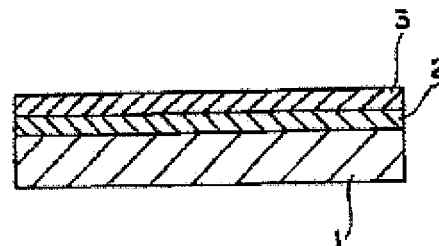
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(54) COATED PLATE WITH HIGH RESISTANCE TO POLLUTION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a coated plate bearing a coating which is formed from a coating material cured and dried at normal temperature and, at the same time, curable by thermal promotion at relatively low temperature and has high surface hardness, weather resistance, durability, and especially high pollution resistance for a long duration.

SOLUTION: This coated plate has a primer layer 2 of an epoxy type primer coating material formed on a substrate 1 and an upper coating layer 3 formed on the primer layer 2 of an upper coating material containing an oligomer solution in which silica of organosilane produced by partial hydrolysis of the hydrolyzable organosilane in colloidal silica is dispersed, polyorganosiloxane containing silanol group, a linear polysiloxane containing hydroxyl groups in both terminals, and a curing catalyst.



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CLAIMS

[Claim(s)]

[Claim 1] It has the primer layer formed from an epoxy system primer paint on the surface of a base material. Are finishing coat formed in the surface of this primer layer from top coat a coated plate which it has, and said top coat, (A_0) General formula $R^1_m SiX_{4-m}(I)$ (among a formula) A monovalent hydrocarbon radical of substitution same $[R^1]$ or of a different kind or the unsubstituted carbon numbers 1-9 is shown, m shows an integer of 0-3 and X shows a hydrolytic basis. A hydrolytic organosilane expressed in colloidal silica distributed by an organic solvent, water, or those mixed solvents. A silica dispersed oligomer solution of an organosilane which carries out partial hydrolysis under conditions which use water 0.001-0.5 mol per said 1 Eq of hydrolytic basis (X)s, (B_0) Average composition formula $R^2_a Si(OH)_b O_{(4-a-b)/2}(II)$ (among a formula) A monovalent hydrocarbon radical of substitution same $[R^2]$ or of a different kind or the unsubstituted carbon numbers 1-8 is shown, a and b are numbers which fill a relation of $0.2 < a < 2$, $0.0001 < b < 3$, and $a+b < 4$, respectively. Polyorganosiloxane which is expressed and contains a silanol group in a molecule, (C_0) Empirical formula $HO(R^2)_n SiO_n$ (among a formula) R^2 --- said formula (II) --- the same as an inner thing --- n --- three or more integers. With a straight-chain-shape both-ends hydroxyl group content polysiloxane (straight-chain-shape polysiloxanediol) expressed, (D_0) Including a curing catalyst, inside of the aforementioned (A_0) ingredient, Said silica is contained five to 95 weight % as solid content, and said at least 50-mol% of hydrolytic organosilane is an organosilane of $m=1$. While the 99 to ingredient 1 aforementioned (B_0) weight section is blended to the one to ingredient 99 aforementioned (A_0) weight section. (However, the total quantity of an ingredient (A_0) and an ingredient (B_0) is 100 It is a weight section) A contamination-resistant coated plate which contains 0.1 to 70 weight % of the aforementioned (C_0) ingredients to the above (A_0), (B_0), and (D_0) sum total solid content of an ingredient

[Claim 2] The contamination-resistant coated plate according to claim 1 in which said base material is an inorganic cured body.
[Claim 3] The contamination-resistant coated plate according to claim 1 in which said base material is a metal plate.
[Claim 4] The contamination-resistant coated plate according to claim 1 in which said base material is a water glass decorative sheet.
[Claim 5] The contamination-resistant coated plate according to claim 1 in which said base material is a plastic-molding board.
[Claim 6] A contamination-resistant coated plate given in either from Claim 1 in which said epoxy system primer paint is an epoxy resin primer paint to 5.
[Claim 7] A contamination-resistant coated plate given in either characterized by comprising the following from Claim 1 to 5.
Said epoxy system primer paint is epoxy resin (A_1) and/or silicone resin modified epoxy resin 100 weight section.

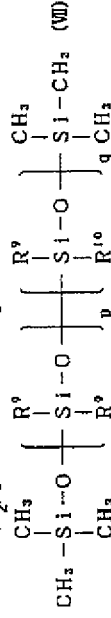
(B_1) At least one hydrolytic basis combined with a silicon atom.
One to hydrolytic organic silicon compound 400 weight section which has at least one isocyanato group and/or an isocyanuric ring which were combined with a silicon atom via at least one carbon atom.
(C_1) 0.01 to curing catalyst 30 weight section, and general formula (D_1) $R^3 R^4 SiY_2(IV)$ (R^3 and R^4 among a formula) Expressing a univalent hydrocarbon group independently, respectively, Y expresses a univalent

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hydrolytic basis. A hydrolytic JIORUGANO silane expressed and/or its one to partial hydrolysis condensate 300 weight section

[Claim 8] Said epoxy system primer paint ((A_2) a) ethylene type monomer 99.5 - 75-mol %, (b) General formula $R^5 SiX_m R^6_{(3-m)}$ (V) (among a formula) R^5 expresses a univalent hydrocarbon group containing a vinyl group, and R^6 expresses a univalent hydrocarbon group of the carbon numbers 1-10, and X, A basis selected from groups which consist of an alkoxyl group of the carbon numbers 1-4, an alkoxy alkoxyl group of the carbon numbers 2-6, and an oxime group of the carbon numbers 2-4 which can be hydrolyzed is expressed, m expresses an integer of 1-3, 0.5-25 mol of unsaturation group content silicon compound % expressed, A hydrolytic basis content vinyl system copolymer produced by making carry out copolymerization, and a ((B_2) c) bisphenol A-epichlorohydrin system epoxy resin, (d) General formula (R^7)

$Si(OR^8)_p O_{cx}(VI)$ (among a formula) R^7 expresses a univalent hydrocarbon group which is mutually the same or different, R^8 expresses a hydrogen atom or a univalent hydrocarbon group, a is the number of 1.0-1.7, b is the number of 0.05-0.2, and c is a number expressed with $(4-a-b)/2$, x is two or more numbers. Epoxy denaturation silicone resin obtained by making polyorganosiloxane expressed react, and a general formula (C_2) [Chemical formula 1]



(R^9 among a formula a univalent hydrocarbon group which is mutually the same or different) [express and] R^{10} expresses a univalent epoxy functional organic group, p is an integer of 0-100, and q is an integer of 1-100. A contamination-resistant coated plate given in either from Claim 1 containing epoxy modified silicone oil expressed and an organic solvent (D_2) to 5.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] In this invention, it is constructed in more detail about a contamination-resistant coated plate at the circumference of a road and the side in a tunnel, the inner surface of a building and an outside surface, a windowpane, and the range of a kitchen, the circumference of a sink, the circumference of a ventilation fan, etc.

Therefore, it is related with the coated plate which demonstrates the resistance to contamination outstanding over the long period of time to exhaust gas, a general pollutant, scribble of a car, etc.

[0002]

[Description of the Prior Art] Conventionally, the coated steel sheet of a high durability paint (a fluorine system, an acrylic silicon system) and the decorative sheet which applied water glass are generally well known as an example of representation of the coated plate constructed on a road and the side in a tunnel, the inner surface of a building, and an outside surface. As compared with the conventional organic paint coated steel sheet, the coated steel sheet of this high durability paint has good weatherability, and it is excellent in water repellence, protection against dust nature, and a mold-release characteristic. However, once it is polluted so that it may be inferior to long-term performance maintenance and may be represented by rain Jimi etc., it will become dirty, and omission has the fault that it is very bad. Since the surface hardness of a coat is low, when it constructs on a road, a crack enters easily with a pebble etc. and it also has the fault of producing degradation from there. Since the decorative sheet which applied water glass has very high surface hardness, a crack cannot enter easily and it is constructed by many roads and tunnel now, but resistance to contamination is dramatically low. In the case of manufacture of a decorative sheet, in order to apply water glass to a base material, it must print at an elevated temperature, and if a production line with oven is not used, it cannot manufacture.

[0003] Many things which performed hard court processing and endurance processing on the plastic-molding board have appeared on the market to the general market in recent years. They are a hard court of the **** and a polycarbonate sheet, and the polyester film which carried out the surface treatment. However, since said hard court has too high surface hardness, it produces a crack easily in small stress. If it results in said film, the commercial item of a contamination-resistant use has few numbers, and, moreover, a film's own endurance is dramatically low.

[0004] On the other hand, the silicone resin composition is known as a room-temperature-setting type coating material excellent in weatherability (for example, refer to JP.S56-15827B). The cured coating of this silicone resin composition has dramatically outstanding solvent resistance, a mold-release characteristic, water repellence, and heat resistance. However, the pencil hardness has only 2H and a crack will enter easily with a pebble etc.

[0005] It has a siloxane bond as a main skeleton, and what is indicated by JP.H4-175388A is known as a room-temperature-setting type coating material which excels said high durability paint in weatherability further, however, although weatherability and surface hardness are boiled markedly and it excels, about resistance to contamination, it cannot be said that it excels dramatically.

[0006]

[Problem to be solved by the invention] While carrying out the dry hard of the purpose of this invention at ordinary temperature, comparatively, hardening by the promotion of heating in low temperature is also formed from a possible paint, and its surface hardness is high, and there is in providing the coated plate which has the coating film which it not only excels in weatherability and endurance, but was excellent in

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resistance to contamination over especially the long period of time in the outermost surface.

[0007]

[Means for solving problem] The contamination-resistant coated plate concerning this invention has the primer layer formed from the epoxy system primer paint on the surface of the base material, and has the finishing coat formed in the surface of this primer layer from top coat. Said top coat is general formula (A_0)

$R^1_m SiX_{4-m}(I)$ (among a formula). The monovalent hydrocarbon radical of substitution same $[R^1]$ or of a different kind or the unsubstituted carbon numbers 1-9 is shown, m shows the integer of 0-3 and X shows a hydrolytic basis. The hydrolytic organosilane expressed in the colloidal silica distributed by an organic solvent, water, or those mixed solvents. The silica dispersed oligomer solution of an organosilane which carries out partial hydrolysis under the conditions which use water 0.001 -0.5 mol per said 1 Eq of hydrolytic basis (X)s. (B_0) Average composition formula $R^2_a Si(OH)_b O_{(4-a-b)/2}(II)$ (among a formula) The

monovalent hydrocarbon radical of substitution same $[R^2]$ or of a different kind or the unsubstituted carbon numbers 1-8 is shown, a and b are numbers which fill the relation of $0.2 < a < 2$, $0.0001 < b < 3$, and $a+b < 4$, respectively. Polyorganosiloxane which is expressed and contains a silanol group in a molecule, (C_0) Empirical formula $HO(R^2)_2 SiO_n H$ (III) (the inside of a formula and R^2 are said formula (II)s it is the same as

an inner thing, and n is three or more integers. The straight-chain-shape both-ends hydroxyl group content polysiloxane (straight-chain-shape polysiloxanedio) expressed, (D_0) Including a curing catalyst, inside of the aforementioned (A_0) ingredient, Said silica is contained five to 95weight % as solid content, and said at least 50-mol% of hydrolytic organosilane is an organosilane of $m=1$. While the 99 to ingredient 1 aforementioned (B_0) weight section is blended to the one to ingredient 99 aforementioned (A_0) weight section. (However, the total quantity of an ingredient (A_0) and an ingredient (B_0) is 100 It is a weight section) 0.1 to 70 weight % of the aforementioned (C_0) ingredients are blended to the above (A_0), (B_0), and (D_0) the sum total solid content of an ingredient.

[0008] Although limitation in particular is not carried out, as a base material used by this invention A local street, a highway, and the side of a tunnel. When constructing to the circumference of internal and external surfaces of a building, a windowpane, and a range of a kitchen, the circumference of a sink, a circumference of a ventilation fan, etc., an inorganic cured body from a viewpoint that it can attach easily, a metal plate, a water glass decorative sheet, a plastic-molding board, etc. are preferred.

[0009] With said inorganic cured body, for example JIS-A5430 fiber reinforced cement plate, JIS-A5422 ceramic-industry system siding, JIS-A5404 cemented excelsior board, JIS-A5414 pulp cement board, JIS-A5426 slate and a wood wool cement laminate sheet, JIS-A6901 plaster-board products, JIS-A5208 clay roofing tile, JIS-A5402 pressed cement roof tile, JIS-A5209 clay tile, a JIS-A5406 structural concrete block. The base material at large which made inorganic materials, such as JIS-A5411 terrazzo, a JIS-A5412 prestressed-concrete double T slab, JIS-A5416 ALC panel, JIS-A6511 hollow prestressed concrete panel, and JIS-RI250 common brick, harden and fabricate is pointed out.

[0010] With said metal plate, for example JIS-G3302 hot-dip zinc-coated carbon steel sheet, JIS-G4304, G4305 rolling aluminum alloy, A metal plate JIS-G3302 hot-dip zinc-coated carbon steel sheet, JIS-G4304, G4305 rolling stainless steel plate, JIS-G3303 tin sheet, and at large [other] is pointed out. Said water glass decorative sheet refers to the decorative sheet etc. which applied sodium silicate to cement base materials, such as a slate, and printed it, for example.

[0011] Said plastic-molding board refers to what fabricated thermosetting plastic, thermoplastics, fiber reinforced plastics, etc. to a sheet shaped or film state, for example. Although a base material with many voids is often shown in the surface in an inorganic cured body, when it is such a base material, it is possible to consider it as a base material without a void by the surface being filled up with polymer cement or putty. In that case, it cannot be overemphasized that the primer used for this invention sticks on polymer cement or putty.

[0012] In the case of the water glass decorative sheet, have come out to the commercial scene as a tunnel inner package board as it is now, but. The contamination-resistant coated plate which could give the contamination-resistant function and was dramatically rich in endurance from the endurance of the decorative sheet itself by applying further to the surface of this decorative sheet the primer paint and top coat which are used for this invention can be created. As an epoxy system primer paint used by this invention, although limitation in particular is not carried out, the 1st, 2nd, and 3rd epoxy system primer

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paints etc. that are described below are mentioned, for example.

[0013] Said 1st epoxy system primer paint refers to an epoxy resin primer paint, and as the example, A commercial solvent system two-component type epoxide primer, a solvent system two-component type epoxy sealer, a drainage system two-component type epoxy emulsion primer, a drainage system two-component type epoxy emulsion sealer, etc. are mentioned. Said 2nd epoxy system primer paint Epoxy resin (A₁) and/or silicone resin modified epoxy resin 100 weight section, (B₁) At least one hydrolytic basis combined with the silicon atom. One to hydrolytic organic silicon compound 400 weight section which has at least one isocyanato group and/or isocyanuric ring which were combined with the silicon atom via at least one carbon atom, (C₁) 0.01 to curing catalyst 30 weight section, and general formula (D₁) R³R⁴SiY₂ (IV) (R³ and R⁴ among a formula) Expressing a univalent JIORUGANO silane independently, respectively, Y expresses a univalent hydrolytic basis. The hydrolytic JIORUGANO silane expressed and/or its one to partial hydrolysis condensate 300 weight section are included.

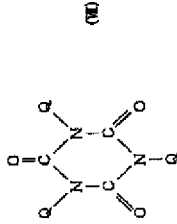
[0014] The aforementioned (A₁) ingredient is an ingredient which gives a strong adhesive property to the 2nd epoxy system primer paint. The epoxy resin used as the aforementioned (A₁) ingredient is defined as the epoxy compound which has two or more epoxy groups in a molecule, and means from a low-molecular thing to the thing of a high polymer. As such an epoxy resin, although limitation in particular is not carried out. For example, bisphenol A diglycidyl ether and its chain polymer, Tetraabromobisphenol A diglycidyl ether and its chain polymer, Glycidyl ether type epoxy resins, such as bisphenol F diglycidyl ether and phenol novolak type epoxy resin; Phthalic acid diglycidyl ester, Tetrahydrophthalic acid diglycidyl ester, diglycidyl hexahydrophthalate, Glycidyl ester typed epoxy resin, such as 3-methyl diglycidyl hexahydrophthalate; Vinylcyclohexene dioxide, 3,4-epoxycyclohexylmethyl (3,4-epoxy cyclohexane) carboxylate, 3,4-epoxy-6-methylcyclohexylmethyl (3,4-epoxy-6-methylcyclohexane) carboxylate, the liquefied epoxy compound which has two or more epoxy groups which cycloaliphatic epoxy resin, such as bis adipate (3,4-epoxy-6-methylcyclohexylmethyl), etc. are mentioned. In addition are generally used as reactive diluent of an epoxy resin -- for example, Polyethylene glycol diglycidyl ether, Polypropylene glycol diglycidyl ether, butanediol diglycidyl ether, trimethylolpropane triglycidyl ether, glycerol triglycidyl ether, etc. can also be used. Only one sort may be used for these and they may use two or more sorts together.

[0015] A silicone resin modified epoxy resin used as the aforementioned (A₁) ingredient refers to what denaturalized an above-mentioned epoxy resin by polyorganosiloxane resin. While compatibility with the aforementioned (B₁) ingredient becomes a large area more by using a silicone resin modified epoxy resin, ultraviolet rays-proof are improved. What carried out copolycondensation also of what only mixed an epoxy resin and polyorganosiloxane resin in the range which shows compatibility mutually may be sufficient as such a silicone resin modified epoxy resin. A rate with a part for an epoxy resin and silicone resin in a silicone resin modified epoxy resin has preferred within the limits of 30 to 85 weight % of epoxy pitches, and 15 to 70 weight % of silicone pitches on balance of an adhesive property, a water resisting property, and weatherability, although limitation in particular is not carried out.

[0016] A hydrolytic organic silicon compound used as the aforementioned (B₁) ingredient is an ingredient which makes an adhesive property between a primer layer and finishing coat reveal while it reacts to the aforementioned (A₁) ingredient and strengthens more the adhesive property of a primer layer to a base material. As a hydrolytic organic silicon compound which has an isocyanato group, Although limitation in particular is not carried out, for example 3-isocyanato propyltrimethoxysilane, 3-isocyanatopropyl triethoxysilane, 3-isocyanatopropyltris (2-methoxyethoxy) Silang, 3 functionality Silang, such as 3-isocyanatopropyltris (methylalcohol ketoxime) Silang, 3-isocyanato propylmethyl dimethoxysilane, 3-isocyanatopropylmethyl dimethoxysilane, 3-isocyanato propylmethyl diethoxysilane, Isocyanato group content Silang like 2 functionality Silang I, such as 3-isocyanatopropylmethyl diethoxysilane, 1; and isocyanato methyl group content Silang corresponding to these, and 4-isocyanatobutyl group content Silang, etc. are mentioned. These partial hydrolysis condensates can also be used.

[0017] As a hydrolytic organic silicon compound which has an isocyanuric ring, although limitation in particular is not carried out, it is a general formula, for example, [0018]

[Chemical formula 2]



[0019] (Three Q among a formula -R¹¹SiR¹²X_{3-c} group same or of a different kind) [express and] R¹¹

expresses divalent hydrocarbon groups, such as an alkylene group, R¹² expresses a univalent hydrocarbon group, X expresses a univalent hydrolytic basis, and c is an integer of 0-2. What is expressed is mentioned. Among the above-mentioned formula, although limitation in particular is not carried out as R¹¹ and X, what described the ingredient at large previously (B₁) is illustrated. Although limitation in particular is not carried out but a low-grade alkyl group, vinyl groups, etc., such as a methyl group and an ethyl group, are

illustrated as R¹², since composition is easy, a methyl group is preferred. As such a compound, although limitation in particular is not carried out, specifically, each of three Q is 3-(trimethoxysilyl) propyl group, 3-(triethoxy silyl) propyl group, and 3- [Tris(2-methoxyethoxy) silyl] A propyl group, 3- [Tris(methylalcohol ketoxime) silyl] The thing which is a propyl group, 3-(methyl dimethoxy silyl) propyl group, or 3-(methylalcohol ketoxime) silyl] The curing catalyst used as the aforementioned (C₁) ingredient is an ingredient which makes the reaction between the aforementioned (A₁) ingredient and the aforementioned (B₁) ingredient, and each polycondensation reaction perform near ordinary temperature, and stiffens a primer paint. Although limitation in particular is not carried out as such a curing catalyst, calcium hydroxide, Alkali earth metal hydroxide, such as magnesium hydroxide; an inorganic compound like basic metal salt, such as alkali earth metal oxide; basic zinc carbonate, such as a calcium oxide and magnesium oxide, and basic magnesium carbonate, etc. are illustrated.

[0021] As a curing catalyst of another group, diisopropoxy (ethylacetate ASETATO) aluminum, Tris(ethylacetate ASETATO) aluminum, tris(acetylacetate) aluminum, Aluminum chelate compounds, such as bis (ethylacetate ASETATO)acetylacetate aluminum; Aluminum bird isopropoxide, Aluminum alkoxides, such as aluminum tributoxide; Diisopropoxy bis(methylacetate ASETATO)titanium, Diisopropoxy bis(ethylacetate ASETATO)titanium, diisopropoxybis(acetylacetate)titanium, Titanium chelate compound, such as 1,3-propane dioxibis(ethylacetate ASETATO)titanium and tetrakis (acetylacetate) titanium; Tetraisopropoxy titanium, Titanium alkoxides, such as tetra-n-butoxytitanium and tetrakis (2-ethylhexyloxy) titanium; The first tin of isobutyric acid, The first tin of octanoic acid, the first tin of naphthenic acid, the first tin of lauric acid, the first tin of stearic acid, the first tin of oleic acid, the first tin of palmitoleic acid, the first tin of linolic acid, the first tin of beta-benzoylpropionic acid, the first tin of orotic acid, The first tin of cinnamic acid, the first tin of benzoic acid, the first tin of p-bromobenzoic acid, Carboxylic acid tin salt, such as the first tin of phenylacetic acid, and the first tin of tropic acid; a metallic element content organic compound like organotin compounds, such as dibutyltin diacetate, a dibutyltin oct art, and dibutyltin dilaurate, etc. are illustrated.

[0022] As a curing catalyst of another group, 3-aminopropyl trimethoxysilane, 3-aminopropyl triethoxysilane, N-(2-aminoethyl)-3-aminopropyl trimethoxysilane, Amino alkyl alkoxysilane, such as 3-(dimethylamino) propyltrimethoxysilane and 3-aminopropyl methyl dimethoxysilane N-(2-aminoethyl)-3-aminopropyl methyl dimethoxysilane; Carboxylic acid, such as acetic acid or formic acid, Propylamine, 3-methoxypropylamine, 3-ethoxypropylamine, A sec-butylamine, a tert-butylamine, allylamine, 2-ethylhexylamine, diisobutylamine, bis(2-ethylhexyl)amine, A compound like the ammonium salt obtained from organic amine, such as 3-(diethylamino) propylamine and 3-(dibutylamino) propylamine, etc. which have ammonium are illustrated. [0023] One sort of these curing catalysts may be used, or they may use two or more sorts together. The aforementioned (D₁) ingredient is an ingredient which gives the outstanding flexibility which follows expansion and contraction of finishing coat, and bears the primer layer formed at stress by reacting to the aforementioned (A₁) ingredient and/or the aforementioned (B₁) ingredient in the case of hardening of a primer paint. As such (D₁) an ingredient, although limitation in particular is not carried out.

Dimethylmethoxysilane, methylphenyl dimethoxysilane, diphenyldimethoxysilane, JIORUGANO

alkoxysilane, such as dimethyl diethoxysilane, methylphenyl diethoxysilane, and diphenyl diethoxysilane; Dimethylbis(methylethyl ketoxime)Silang, One sort or two sorts or more of partial hydrolysis condensates, JIORUGANOJI ketoxime silanes [, such as methylphenyl bis(methylethyl ketoxime)Silang and diphenylbis (methylethyl ketoxime)Silang,], and these Silang, etc. are illustrated.

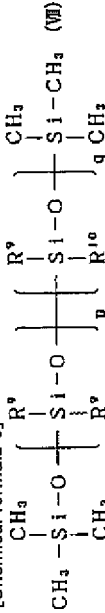
[0024]An organic solvent may be added, in order to dissolve uniformly the above (A₁), (B₁), (C₁), and (D₁) an ingredient and to give good coating operability. Color pigments, such as titanium oxide, carbon black, and iron oxide, a various filler and distribution auxiliary agent, an antioxidant, an ultraviolet ray absorbent, a dripping stop agent, etc. may be added if needed. Said 3rd epoxy system primer paint ((A₂) a) ethylene type monomer 99.5 ~ 75-mol %, (b) General formula R⁵SiX_mR⁶ (3-m) (V) (among a formula) R⁵ expresses the

univalent hydrocarbon group containing a vinyl group, and R⁶ expresses the univalent hydrocarbon group of the carbon numbers 1-10, and X, The basis selected from the groups which consist of the alkoxyl group of the carbon numbers 1-4, an alkoxyl group of the carbon numbers 2-6, and an oxime group of the carbon numbers 2-4 which can be hydrolyzed is expressed, m expresses the integer of 1-3, 0.5-25 mol of unsaturation group content silicon compound % expressed, The hydrolytic basis content vinyl system copolymer produced by making carry out copolymerization, and a ((B₂) c) bisphenol A-epichlorohydrin

system epoxy resin, (d) General formula (R⁷)_aSi(OR⁸)_bO_c (VI) (among a formula) R⁷ expresses the

univalent hydrocarbon group which is mutually the same or different, R⁸ expresses a hydrogen atom or a univalent hydrocarbon group, a is the number of 1.0-1.7, b is the number of 0.05-0.2, and c is a number expressed with (4-a-b) / 2, x is two or more numbers. The epoxy denaturation silicone resin obtained by making the polyorganosiloxane expressed react, and general formula (C₂) [0025]

[Chemical formula 3]



[0026]((R⁸ expresses among a formula the univalent hydrocarbon group which is mutually the same or different, R¹⁰ expresses a univalent epoxy functional organic group, p is an integer of 0-100, and q is an integer of 1-100.) — the epoxy modified silicone oil expressed and an organic solvent (D₂) are included.

[0027]As an ethylene type monomer used as a raw material (a) of the aforementioned (A₂) ingredient,

Although limitation in particular is not carried out, for example Methyl acrylate, methyl methacrylate, Ethyl acrylate, ethyl methacrylate, propylacrylate, Propyl methacrylate, butyl acrylate, butyl methacrylate, Hexyl acrylate, hexyl methacrylate, 2-ethylhexyl acrylate, Alkyl (meta) acrylate, such as 2-ethylhexyl methacrylate; Styrene, Conjugated dienes, such as vinylidene, butadiene, such as vinyl-aromatic-hydrocarbons; VCM/PVC, such as vinyltoluene and alpha-methylstyrene, and a vinylidene chloride, and isoprene; the vinyl ester of the saturated fatty acid of the carbon numbers 1-12 of vinyl acetate, vinyl propionate, etc., etc. are mentioned.

[0028]As an unsaturation group content silicon compound used as a raw material (b) of the aforementioned (A₂) ingredient, Although limitation in particular is not carried out, it is said formula (V), for example. Inner

R⁵ is recommended from the ease of raw material acquisition and composition of what is 3-acryloxypropyl group or 3-methacryloxypropyl group. Said formula (V) As R⁶, an alkyl group or phenyl groups, such as methyl, ethyl, propyl, butyl, pentyl, and hexyl, etc. are recommended from the ease of raw material acquisition and composition inside, and a methyl group is especially preferred from a point of raw material acquisition.

[0029]As said formula (V) Naka and the hydrolytic basis X, Although limitation in particular is not carried out, for example Methoxy and ethoxy **n-propoxy, The alkoxyl group of the carbon numbers 1-4, such as n-butoxy; the oxime group of the carbon numbers 2-4, such as acyloxy group; methylethyl ketoxime of the carbon numbers 2-4, such as alkoxyl group; acetoxy of the carbon numbers 2-6, such as methoxy ethoxyl and ethoxyethoxyl, etc. are mentioned. Although several meters of the hydrolytic basis X are chosen from the integer of 1-3, from the meaning which makes network structure form in the inside of a short time, it is preferred that it is 2 or 3, and it is preferred that it is especially 3.

[0030]As an example of said unsaturation group content silicon compound (b), Although limitation in

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particular is not carried out, 3-acryloxypropyltrimethoxysilane, 3-acryloxypropyltriethoxysilane, 3-acryloxypropyltris (ethoxyethoxy) Silang, 3-acryloxypropyl tris (methylethyl ketoxime) Silang, 3-methacryloxypropyl trimethoxysilane, 3-methacryloxypropyl triethoxysilane, 3-methacryloxypropyl tris (methylethyl ketoxime) Silang, etc. are mentioned.

[0031]The hydrolytic basis content vinyl system copolymer of the aforementioned (A₂) ingredient, Said raw material (a) and (b) is about obtained the temperature from a room temperature to the flowing-back temperature of a solvent, and by carrying out a copolymerization reaction at the temperature of 50-150 ** preferably, for example under existence of an organic solvent and a free radical initiator (radical polymerization initiator). In this reaction, the usable kind and quantity of an organic solvent may be the same as the organic solvent of the ingredient described later (D₂). Although limitation in particular is not carried out as said free radical initiator, can use an azo compound or organic peroxide and, for example specifically, Azobisisobutyronitrile, 1-butyl hydroperoxide, a cumene hydroperoxide, di-t-butyl peroxide, dicumyl peroxide, benzoyl peroxide, t-butyl par benzoate, acetone peroxide, etc. are illustrated. Although limitation in particular is not carried out, 0.01 to 1 weight % is suitable for the quantity of a free radical initiator to a raw material (a) and the total quantity of (b).

[0032]When performing a raw material (a) and the copolymerization reaction of (b), n-propanethiol, The molecular weight of the copolymer to generate is also controllable using chain transfer agents, such as 1-hexanethiol, 1-decanethiol, benzenethiol, 3-mercaptopropyltrimethoxysilane, and 3-mercaptopropyl triethoxysilane. A raw material (a) and the use rate with (b) are as aforementioned. If there is less amount of the raw material (b) used than said range, the adhesive property between finishing coat and a primer layer will fall, and a primer layer will become weak if conversely more than said range.

[0033]As polyorganosiloxane used as a raw material (d) of the aforementioned (B₂) ingredient, Although limitation in particular is not carried out, it is said formula (VI), for example. That etc. whose inner

hydrocarbon-group R⁷ is aryl groups, such as alkanyl-group; phenyls, such as alkyl-group; vinyl, such as methyl, ethyl, propyl, butyl, hexyl, and octyl, and allyl, are mentioned. However, it exceeds in a water resisting property or weatherability, and the polymethyl phenyl siloxane the viewpoints that compatibility with an epoxy resin is good, that composition is easy, etc. to whose R⁷ is mixture with a methyl group and a phenyl group is preferred. Said formula Although limitation in particular is not carried out as an example of (VI)

Naka and R⁸, alkyl groups, such as a hydrogen atom or methyl, ethyl, propyl, or butyl, are mentioned. Said formula (VI) When it is in the tendency for compatibility with the epoxy resin of the polyorganosiloxane which has a moderate degree of polymerization when using it as a is less than 1.0 inside to be inferior and 1.7 is exceeded, there is a possibility that the tough nature of resin coating may fall. If the tough nature of resin coating falls that b is less than 0.05 and 0.2 is exceeded, the tendency which the increase in viscosity and gelling tend to produce during preservation will be seen.

[0034]A bisphenol A-epichlorohydrin system epoxy resin used as a raw material (c) of the aforementioned (B₂) ingredient, Although it is the amount object of low thru/or a polymer containing a compound with oxysilane oxygen, such as a glycidyl group and a 3,4-oxo cyclohexyl group, and various acid anhydrides, amines, etc. may be used as the hardening agent, it is not limited to these but a common hardening agent for epoxy resins can be applied. However, in order to live together in other ingredients and stability in a solution, and to cause hardening near ordinary temperature and to form a film, using an acid anhydride system hardening agent is recommended. As such an acid anhydride, although limitation in particular is not carried out, a phthalic acid anhydride, a maleic acid anhydride, a hexahydrophthalic anhydride, a pyromellitic anhydride, trimellitic anhydride, a dodecyl succinic acid anhydride, etc. are mentioned, for example. A hardening agent may use two or more sorts together, using only one sort.

[0035]As for the amount of the aforementioned (B₂) ingredient used, although limitation in particular is not carried out, it is preferred that they are 100 or less weight sections as solid content to the ingredient 100 aforementioned (A₂) weight section. (B₂) If the amount of ingredient used exceeds 100 weight sections, an adhesive property will fall. General formula (VII) of epoxy modified silicone oil which is the aforementioned (C₂) ingredient as an example of R⁹, inside, Although limitation in particular is not carried out, aryl groups, such as alkyl-group; phenyls, such as methyl, ethyl, propyl, butyl, hexyl, and octyl, and tolyl, etc. are mentioned. Although limitation in particular is not carried out as an example of R¹⁰, an organic group etc. which have a glycidyl group, a glycidioxy group, a 3,4-epoxycyclohexyl group, a 2,3-epoxycyclopentyl group, etc. are illustrated.

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[0036] Especially the epoxy modified silicone oil that is the aforementioned (C_2) ingredient is obtained by carrying out the addition reaction (hydrosilylation) of the olefin nature epoxy monomer to a polymethyl hydrogen siloxane, for example, although not necessarily limited. The amount of the epoxy modified silicone oil used is 0.1 to 50 weight % of within the limits to the sum total solid content of the aforementioned (A_2) ingredient and an ingredient (B_2) preferably, although limitation in particular is not carried out. If sufficient adhesion with a base material is not acquired as it is less than 0.1 weight %, but it exceeds 50 weight %, the hardenability of a primer will fall.

[0037] As an organic solvent used as the aforementioned (D_2) ingredient, Although limitation in particular is not carried out, for example Methyl alcohol, ethyl alcohol, Alcohols, such as isopropyl alcohol; Ethylene glycol monomethyl ether, Ether alcohol or ether, such as ethylene glycol monoethyl ether, a tetrahydrofuran, and dioxane; Ketone, such as methyl ethyl ketone and a diethyl ketone; Methyl acetate, Aliphatic hydrocarbon, such as ester species; n-hexane, such as ethyl acetate and n-butyl acetate, gasoline, a rubber solvent, a mineral spirit, and kerosene; aromatic hydrocarbon, such as benzene, toluene, and xylene, is mentioned.

[0038] The amount of the aforementioned (D_2) ingredient used has preferred within the limits of ten to 5000 weight section to the ingredient 100 aforementioned (A_2) weight section, although limitation in particular is not carried out. Since it will be necessary to give two coats repeatedly if workability falls and 5000 weight sections are exceeded, since the viscosity of a primer paint will become high if there is less amount used than 100 weight sections, workability falls too.

[0039] A curing catalyst can be used to harden at ordinary temperature when you want to burn for a short time, the case where he would like to print comparatively the 3rd epoxy system primer paint containing these (A_2) (B_2), (C_2), and an ingredient (D_2) at low temperature, and. As for the amount of the curing catalyst used, although limitation in particular is not carried out, it is preferred that they are less than 30 weight sections to the ingredient 100 aforementioned (A_2) weight section. If the amount of the curing catalyst used exceeds 30 weight sections, foaming is produced at the time of baking of a primer paint, or a curing catalyst will ooze on the surface of primer cured coating, and an adhesive property with finishing coat will be checked. Although limitation in particular is not carried out, as an example of a curing catalyst

Dibutyltin dilaurate, Dibutyltin diacetate, a butyltin bird (2-ethylhexoate). The 1st tin of caprylic acid, naphthenic acid tin, oleic acid tin, iron-2-ethylhexoate, Lead-2-ethyl octoate, cobalt 2-ethylhexoate, Manganese 2-ethylhexoate, zinc-2-ethylhexoate, Organic-carboxylic-acid metal salt, such as naphthenic acid titanium, zinc naphthenate, cobalt naphthenate, and zinc stearate; Tetrabutyl titanate, Tetra (2-ethylhexyl) titanate, triethanolamine titanate, Organic titanium acid ester, such as tetra (isopropenyl) titanate; ORGANO siloxy titanium, Organic titanium compounds, such as beta-carbonyl titanium; gamma-aminopropyl triethoxysilane, Amino alkyl-group substitution alkoxysilane, such as N-(trimethoxysilylpropyl) ethylenediamine; Hexylamine, amine compounds, such as phosphoric acid dodecyl amine, or salt; --- 4th ammonium salt [, such as benzyl triethyl ammonium acetate,], --- potassium acetate and sodium acetate. The lower-fatty-acid salt of alkaline metals, such as a lithium oxalate; Dimethylhydroxylamine, Dialkyl hydroxylamine, such as diethylhydroxylamine; guanidine compounds, such as tetramethyl guanidine, and guanidyl group content Silang, or a siloxane compound can be mentioned.

[0040] Said 3rd epoxy system primer paint may contain further color pigments, such as titanium oxide, carbon black, and iron oxide, a various filler and distribution auxiliary agent, an antioxidant, an ultraviolet ray absorbent, a dripping stop agent, etc. if needed. Silica distribution oligomer which is an ingredient (A_0) of the top coat used by this invention, To for example, the colloidal silica distributed by an organic solvent or water (the mixed solvent of an organic solvent and water is also included). One sort of the hydrolytic organosilane expressed with said general formula (I) or two sorts or more are added, It is water 0.001-0.5 per said 1 Eq of hydrolytic basis (X)s about the water or the water added separately in colloidal silica. It is obtained by carrying out partial hydrolysis of this hydrolytic organosilane under the conditions which use a mol.

[0041] As basis R^1 in the hydrolytic organosilane expressed with said general formula (I). Although limitation in particular is not carried out, for example A methyl group, an ethyl group, a propyl group, Alkyl groups, such as a butyl group, a pentyl group, a hexyl group, a heptyl group, and an octyl group; A cyclopentyl group, Cycloalkyl groups, such as a cyclohexyl group; 2-phenylethyl group, Aralkyl groups, such as 2-phenylpropyl group and 3-phenylpropyl group; A phenyl group, Aryl groups, such as a tolyl group; Alkenyl-group; chloromethyl groups, such as a vinyl group and an allyl group, Halogenation hydrocarbon-

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group; gamma-methacryloxypropyl groups, such as gamma-chloropropyl group and a 3,3,3-trifluoropropyl group, Substitution hydrocarbon groups, such as gamma-glycidox propyl group, a 3,4-epoxycyclohexyl ethyl group, and gamma-mercaptopropyl group, etc. can be illustrated. Also in these, the alkyl group of a composite ease or the ease of acquisition to the carbon numbers 1-4 and a phenyl group are preferred. [0042] Although limitation in particular is not carried out as said general formula (I) Naka and the hydrolytic basis X, an alkoxy group, an acetoxy group, an oxime group, an ENOKISHI group, an amino group, aminoxy, an amide group, etc. are mentioned, for example. Also in these, since it is easy to prepare an ease of acquisition, and a silica distribution organosilane oligomer solution, an alkoxy group is preferred.

[0043] As an example of said hydrolytic organosilane, The alkoxysilane of each functionality of mono-, di-, tri-, and tetra- whose m of said general formula (I) Naka is an integer of 0-3, acetoxy silane, oxime silanes, hackberry gardenia fruit orchid species, aminosilanes, friend NOKISHI silanes, and amide silanes are mentioned. Also in these, since it is easy to prepare an ease of acquisition, and a silica distribution organosilane oligomer solution, alkoxysilane is preferred.

[0044] Especially as tetra alkoxy silane of $m=0$, Can illustrate a tetramethoxy silane, a tetraethoxysilane, etc. and as organotrialkoxy silane of $m=1$, Methyl trimethoxysilane, methyl triethoxysilane, a methyl triisopropoxy silane, phenyltrimethoxysilane, phenyltriethoxysilane, 3 and 3, 3-trifluoropropyl trimethoxysilane, etc. can be illustrated. As a JIORUGANO dialkoxo silane of $m=2$, Dimethyldimethoxysilane, dimethyl diethoxysilane, diphenyldimethoxysilane, Can illustrate diphenyl diethoxysilane, methylphenyl dimethoxysilane, etc. and as bird organoalkoxy silane of $m=3$, Trimethylmethoxysilane, trimethylethoxysilane, trimethyl isopropoxy silane, dimethylisobutyl methoxysilane, etc. can be illustrated. An organosilane compound generally called a silane coupling agent is also contained in alkoxysilane.

[0045] The inside of the hydrolytic organosilane expressed with said these general formula (I)s, and more than 50 mol % --- desirable --- 60-mol % --- the above --- more --- desirable --- 70-mol % --- the above is trifunctional [which is expressed with $m=1$]. This is 50-mol % Dry hardenability is easily inferior while film hardness sufficient in the following is not obtained. As colloidal silica in the aforementioned (A_0) ingredient,

although limitation in particular is not carried out, it can use organic solvent dispersibility colloidal silica of non-drainage systems, such as water dispersibility or alcohol, for example. Generally, such colloidal silica is 20 to 50 weight % about the silica as solid content. It contains and silica loadings can be determined from this value. When using water dispersibility colloidal silica, the water which exists as ingredients other than solid content can be used for hydrolysis of said hydrolytic organosilane. Water dispersibility colloidal silica can usually be easily obtained as a commercial item, although made from water glass. Organic solvent dispersibility colloidal silica can be easily prepared in replacing the water of said water dispersibility colloidal silica by an organic solvent. Such organic solvent dispersibility colloidal silica as well as water dispersibility colloidal silica can be easily obtained as a commercial item. The kind of organic solvent which colloidal silica is distributing, Although limitation in particular is not carried out, for example Methanol, ethanol, isopropanol, Lower aliphatic alcohol, such as n-butanol and isobutanol; Ethylene glycol, Ethylene glycol derivatives, such as ethylene glycol monobutyl ether and acetic acid ethylene glycol monoethyl ether; A diethylene glycol, Diethylene-glycol derivative [, such as diethylene-glycol monoethyl ether,], diacetone alcohol, etc. can be mentioned, and one sort chosen from the group which consists of these, or two sorts or more can be used. It can use together with these hydrophilic organic solvents, and toluene, xylene, ethyl acetate, butyl acetate, methyl ethyl ketone, methyl isobutyl ketone, methylethyl ketoxime, etc. can be used.

[0046] Colloidal silica is [be / it / under / aforementioned (A_0) ingredient / setting] a part for silica (weight which converted content Si into SiO_2). It is considered as solid content and contains by 20 to 85 weight % of within the limits more preferably ten to 90 weight % five to 95 weight %. If content is less than 5 weight %, desired film hardness will not be obtained, but on the other hand, when 95 weight % is exceeded, the uniform dispersion of silica may become difficult and an ingredient (A_0) may gel.

[0047] 0.001-0.5 per Eq of hydrolytic basis (X) in which said hydrolytic organosilane has the quantity of the water used when preparing silica distribution oligomer which is the aforementioned (A_0) ingredient as mentioned above. It is within the limits which is a mol. The amount of the water used is 0.001. If sufficient partial hydrolysis is not obtained as it is less than a mol, but 0.5 mol is exceeded, the stability of a partial hydrolysis will worsen. What is necessary is not to limit the method in particular of carrying out partial hydrolysis, for example, to mix a hydrolytic organosilane and colloidal silica, and just to carry out addition combination of the water of an initial complement, and a partial hydrolysis reaction advances at ordinary temperature in that case. In order to promote a partial hydrolysis reaction Chloride, acetic acid,

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halogenation Silang. Organic acid and inorganic acid, such as chloroacetic acid, citrate, benzoic acid, dimethylmalonic acid, formic acid, propionic acid, a glutaric acid, glycolic acid, maleic acid, malonic acid, toluenesulfonic acid, and oxalic acid, may be used as a catalyst.

[0048]In order that the aforementioned (A_0) ingredient may obtain the performance by being stabilized over a long period of time — the pH of liquid — desirable — 2.0–7.0 — more — desirable — 2.5–6.5 — it is good to use 3.0–6.0 still more preferably. Especially the amount of the water used is 0.3 per hydrolytic basis (X) 1 equivalent as pH is outside this range. The fall of the performance durability of an ingredient (A_0) is remarkable under the conditions more than a mol (A_0). What is necessary is for what is necessary to be to add basic reagents, such as ammonia and ethylenediamine, and just to adjust pH, if it is an acidity side, and just to adjust pH using acid reagents, such as chloride, nitric acid, and acetic acid, from this range, if it is a basicity side when pH of an ingredient is outside a mentioned range. However, the adjustment method in particular is not limited.

[0049]As R^2 in said average composition formula (II) of the silanol group content polyorganosiloxane used as the aforementioned (B_0) ingredient, it is not carried out but especially limitation is said formula (I).

Although the same thing as inner R^1 is illustrated, desirable — substitution hydrocarbon groups, such as the alkyl group of the carbon numbers 1–4, a phenyl group, a vinyl group, gamma-glycidioxy propyl group, gamma-methacryloxypropyl group, gamma-aminopropyl group, and a 3,3,3-trifluoropropyl group, — they are a methyl group and a phenyl group more preferably. The inside of said formula (II), and a and b are numbers which fill the aforementioned relation, respectively, and a is 0.2. If the following or b exceeds 3, it will be easy to produce a crack in cured coating. When a is four or less [2 or more], hardening of b does not advance well by less than 0.0001.

[0050]Such silanol group content polyorganosiloxane, although not necessarily limited especially — methyltrichlorosilane, dimethyldichlorosilane, phenyltrichlorosilane, and diphenyl dichlorosilane — or, it can obtain by hydrolyzing one sort or two sorts or more of mixtures of alkoxysilane corresponding to these with a lot of water by a publicly known method. In order to obtain silanol group content polyorganosiloxane, when alkoxysilane is used and it hydrolyzes by a publicly known method, the alkoxy group which is not hydrolyzed may remain in a minute amount. That is, in this invention, although the polyorganosiloxane that a silanol group and a little alkoxy groups live together may be obtained, even if it uses such polyorganosiloxane, it does not interfere.

[0051]Said empirical formula (III) showing the straight-chain-shape both-ends hydroxyl group content polysiloxane (straight-chain-shape polysiloxanediol) which is the aforementioned (C_0) ingredient — inside, although n is as aforementioned, it is within the limits of 10–200 (about about 1000 to 20000 weight average molecular weight) preferably. As a curing catalyst which is the aforementioned (D_0) ingredient, For example, alkyl titanates; Tin octylate, dibutyltin dilaurate, Carboxylic acid metal salt, such as dioctyl tin dimaleate; dibutyl amine 2 — HENKSOETO, Carboxylic acid quaternary ammonium salt, such as amine salt; acetic acid tetramethylammonium, such as dimethylamine acetate and ethanolamine acetate; Amines, such as tetraethyl pentamine, Amine system silane coupling agents, such as N-beta-aminocetyl gamma-aminopropyl trimethoxysilane and N-beta-aminocetyl gamma-aminopropyl methyl dimethoxysilane; P-toluenesulfonic acid, Aluminum compounds, such as acids; aluminum alkoxides, such as phthalic acid and chloride, and aluminum chelate; The alkali catalyst of a potassium hydrate etc., Titanium compounds, such as tetraisopropyl titanate, tetrabutyl titanate, and titanium tetra acetylacetonate; halogenation Silang, such as methyltrichlorosilane, dimethyldichlorosilane, and trimethylmono chlorosilane, is mentioned. However, if effective in condensation of the above (A_0), (B_0), and (C_0) an ingredient, there will be no restriction in particular.

[0052]A blending ratio between the aforementioned (A_0) ingredient and the aforementioned (B_0) ingredient is as aforementioned. (A_0) If there are too many blending ratios of an ingredient, it will be easy to produce a crack on a film, and if too small, sufficient room-temperature-setting performance and film hardness will not be obtained. Loadings of the aforementioned (C_0) ingredient are within the limits of the above. When loadings are less than said range, a contamination-resistant manifestation is weak, if it exceeds said range, hardening will not advance well, therefore a film will become soft.

[0053]An addition of the aforementioned (D_0) ingredient is the total quantity 100 of the aforementioned (A_0) ingredient and the aforementioned (B_0) ingredient, although limitation in particular is not carried out As opposed to a weight section, Within the limits of 0.0005 to 8 weight section is [within the limits of

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0.0001 to 10 weight section] within the limits of 0.0007 to 5 weight section still more preferably more preferably. When an addition may not harden at ordinary temperature at less than 0.0001 weight sections and ten weight sections are exceeded, heat resistance and weatherability may worsen.

[0054]Top coat used by this invention can be diluted and used with various organic solvents, in order to make the handling easy. Although a kind of organic solvent used can be selected with a kind of monovalent hydrocarbon radical of each ingredient, or a size of a molecular weight and limitation in particular is not carried out, what was mentioned above as a dispersing solvent of colloidal silica is mentioned, for example. [0055]In said top coat, paints may be added if needed. As paints which can be added, although limitation in particular is not carried out, for example Carbon black, It does not interfere, even if inorganic pigments, such as organic colors, such as Quinacridone, naphthol red, cyanine blue, cyanine green, and Hansa yellow, titanium oxide, barium sulfate, rouge, and a composite metal oxide, are good and use it combining one sort chosen from these groups, or two sorts or more. What is necessary is just to perform distribution of paints by the usual method. In that case, use of a dispersing agent, a distributed auxiliary agent, a thickening agent, a coupling agent, etc. is possible. A leveling agent, a color, aluminum paste, glass frit, a metal powder, an antioxidant, an ultraviolet ray absorbent, etc. may be added if needed.

[0056]Although for the thickness of the film formed from said top coat not to have restriction in particular and what is necessary is just 0.1 – 200 μm , in order to be stuck to a film, to hold it stably in the long run and for neither a crack nor exfoliation to occur, 10 – 100 μm is preferred. Said top coat can be coated with the usual coating method, for example, can choose the various coating methods of brush coating, a spray, immersion, a flow, a roll, a curtain, a knife coat, etc. Restriction in particular does not have a dilution rate in an organic solvent, and it should just determine a dilution rate if needed.

[0057]Although said top coat can be stiffened at ordinary temperature, heat cure of it may be carried out from relations, such as a production process of a coated plate, if needed. Baking temperature in that case has preferred within the limits of 40 – 200 $^{\circ}\text{C}$, although limitation in particular is not carried out. In a coated plate concerning this invention, since finishing coat is formed from top coat containing said specific ingredient, resistance to contamination excellent in a coated plate is given.

[0058]A straight-chain-shape both-ends hydroxyl group content polysiloxane (straight-chain-shape polysiloxanediol) which is an ingredient (C_0) gives resistance to contamination excellent in a film formed especially among ingredients contained in said top coat. Since this (C_0) ingredient does not have any reaction groups other than an end OH radical, it is a molecule comparatively lacking in reactivity. Therefore, since perfect compatibility in inside of a paint is missing and it is distributing as an ultrathin particle, it gathers in a paint film surface easily, and a monomolecular layer is formed, but eventually, the end OH carries out a condensation reaction to OR group of bulk, and remains in a paint film surface. As a result, since a R^2 group covers a paint film surface and a pollutant (a gas, a solid, a liquid) is not allowed to come near, resistance to contamination is raised by leaps and bounds. Since a R^2 group has covered a paint film surface, even when a pollutant adheres, it makes it possible to remove it easily (decontamination nature is high), and a mold-release characteristic over adhesives etc. is given. Therefore, while being able to remove dirt of dust, etc., such as adhesion and scribble, easily, there is an effect also in prevention of a poster etc. Said empirical formula (III) of an ingredient (C_0) Inner n is able for a large thing to form a layer in a paint film surface in a small quantity. On the other hand, n gives pliability to a coat by it not only forming a layer, but a small thing having the high reactivity of an end OH radical, and being easily incorporated into bulk in a paint film surface, and it leads also to a crack preventive effect. Therefore, a coat where a crack could not enter easily and which was excellent in resistance to contamination by blending optimum dose with top coat from a large thing of n to a small thing as an ingredient (C_0) is formed.

[0059]Said top coat contains (A_0), (B_0), and (D_0) an ingredient in addition to an ingredient (C_0). (A_0) Silica distribution oligomer which is an ingredient. On the occasion of film formation, become the hydrolytic basis as a functional group kept for a hardening reaction the main ingredients of the base polymer which it has, and colloidal silica in (A_0) ingredient. While making hardness of the film formed high, improve the smooth nature of a film, and crack resistance and the silanol group content polyorganosiloxane which is; (B_0) ingredient, (A_0) With an ingredient and (C_0) an ingredient, carry out a condensation reaction and it participates in cured coating formation. The smooth nature, the mechanical strength, and toughness of a film are raised, and the curing catalyst which is; (D_0) ingredient promotes the condensation reaction of the

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of 47.3% and $m=1$ A mol % (A_0-2) (preparation of ingredient) Sand grinder is used, The white paint (A_0-2) (ingredient) was obtained by distributing 20 copies of white pigments ("R820" by Ishihara Sangyo Kaisha, Ltd.) in 100 copies of aforementioned (A_0-1) ingredients.

(A_0-3) an agitator and warming — in the flask furnished with a jacket, a capacitor, and a thermometer (preparation of an ingredient), isopropyl alcohol distribution colloidal silica — sol — IPA-ST (the particle diameter 10-20 — m micro) 30% of solid content, moisture 0.5 %, Nissan Chemical Industries, Ltd. make 100 copy, 68 copies of methyl trimethoxysilane, 18 copies of dimethyldimethoxysilane, and water 8.1 A part and acetic anhydride 0.1 After performing a partial hydrolysis reaction over about 3 hours at the temperature of 80 **, supplying and stirring a part, the reaction mixture was obtained by cooling. Solid content: when this thing was allowed to stand at the room temperature for 48 hours was 38%. The brown paint (A_0-3) (ingredient) was obtained by distributing 15 copies of brown pigments (KN-V by Toda Kogyo Corp.) with a paint shaker in 100 copies of this reaction mixture.

[0076]

(A_0-3) preparation conditions of an ingredient: the number [] of mols of the water per 1 Eq of — hydrolytic bases — silica part content [] of 0.3 and (A_0-3) an ingredient — mol % 77-mol% of the hydrolytic basis content organosilane of 40.2% and $m=1$ — next, (B_0) The example of the preparing method of an ingredient is explained.

[0077](B_0) (example of preparation of an ingredient)

(B_0-1) an agitator and warming — a jacket and a capacitor — (preparation of an ingredient). A mixture of methyl trisopropoxy silane 220 part (1 mol) and toluene 150 part is taught to a flask furnished with a dropping funnel and a thermometer, and it is the 1% hydrochloric acid aqueous solution 108 to this mixture. A part was dropped over 20 minutes and a methyl trisopropoxy silane was hydrolyzed. When stirring was stopped 40 minutes after dropping, it separated into a bilayer. Mixed liquor of lower layer water and isopropyl alcohol having contained a small amount of chlorides is separated. After washing in cold water removing chloride which remains in a resin solution of toluene which remained behind and carrying out decompression removal of the toluene further, by diluting with isopropyl alcohol. An isopropyl alcohol 40% solution (B_0-1) (ingredient) of silanol group content organopolysiloxane of the weight average molecular weight 2,000 [about] was obtained.

(B_0-2) By the same operation as a preparing method of the aforementioned (B_0-1) ingredient, a toluene solution of silanol group content organopolysiloxane was obtained except having changed the last diluent solvent into toluene (preparation of an ingredient). Then, a toluene 40% solution (B_0-2) (ingredient) of silanol group content organopolysiloxane of the weight average molecular weight 10,000 [about] was obtained by performing a dehydrating condensation reaction of silanol group content organopolysiloxane at temperature of 150 ** for 12 hours.

(B_0-3) an agitator and warming — a jacket and a capacitor — (preparation of an ingredient). To the flask furnished with a dropping funnel and a thermometer, it is the water 1,000. Part, Prepare 50 copies of acetone and further 44.8 copies (0.3 mol) of methyltrichlorosilanes, It is the toluene 200 about 38.7 copies (0.3 mol) of dimethyldichlorosilanes, and 84.6 copies (0.4 mol) of phenyltrichlorosilanes. It was dropped under stirring of what was dissolved in the part, and the hydrolysis reaction was performed. After stopping stirring 40 minutes after dropping, moving reaction mixture to a separating funnel and settling it. By removing the water and chloride which carry out liquid separation removal of the lower layer hydrochloric acid water divided into the bilayer, next remain in the toluene solution of the upper organopolysiloxane with superfuous toluene by decompression stripping. The toluene 60% solution (B_0-3) (ingredient) of silanol group content organopolysiloxane of the weight average molecular weight 3,000 [about] was obtained. In the above-mentioned preparing method, a molecular weight is GPC (gel permeation chromatography) (measuring-apparatus species name: HLC-8020, TOSOH CORPORATION make). It is the weight average molecular weight of the standard polystyrene conversion searched for. Future molecular weights were also measured in the similar way.

(C_0) (ingredient) : — said formula (III) — straight-chain-shape polysiloxanediol (polydimethyl siloxane diol) which R^2 is CH_3 inside and has the weight average molecular weight (Mw) shown in Tables 1 and 2.

[0078]

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(D_0) (ingredient) : N-beta-aminoethyl gamma-aminopropyl methyl dimethoxysilane or N-beta-aminoethyl gamma-aminopropyl triethoxysilane.

(Preparing method of top coat) By the combination shown in Tables 1 and 2, top coat was obtained by carrying out mixed stirring of the above (A_0), (B_0), (C_0), and (D_0) the ingredient.

(Coating method of top coat) All were painted with the air spray (coating pressure of 2.5 kg / cm²; the Iwata spray gun W-88 (H5) is used).

(Dry curing method of top coat)

Embodiments 1-5: Ordinary temperature dry hardening (for about 20 ** and three days).

[0079]

Embodiments 6-8: Stoving hardening (for 90 ** and 20 minutes).

(Valuation method of a contamination-resistant coated plate) The method shown below estimated the contamination-resistant coated plate, and the result was shown in Tables 1 and 2.

[0080](1) The 1 contamination method of contamination-resistant ***** : 24-hour neglect after writing a character by oily magic.

Valuation method: Visual observation of the adhesion grade of magic and the state of a character was carried out, and the following three-stage estimated.

O : magic is crawled and it cannot read as a character.

[0081]**: Although magic is crawled, it can read as a character.

x: Magic is not crawled but a character can also be deciphered clearly.

(2) Two coated plates of contamination-resistant ***** were installed to the 30-degree inclination exposure test fence, and the direct weathering test was done.

Exposure conditions: For south, a 30-degree inclination (JIS).

[0082]Valuation method: By a color difference meter, it is a colorimetry (XYZ display) about a coated plate.

Y value [before exposure] (first stage): — Y value after a Y_0 atmospheric exposure test : Y contamination rate : if $D = D - (1 - Y/Y_0) \times 100$ — the soiling degree of a coated plate is expressed by this formula, and a soiling degree is so low that a D value is small. The result of the contamination rate six months after exposure was shown in Tables 1 and 2.

[0083](3) Magic was wiped off with the dry waste cloth after the stain testing by the oily magic tried with the 1 above (1) of decontamination ***** and visual observation of the remaining condition of the magic marker was carried out. A result is based on the following three-stage evaluation.

O : a magic marker can be wiped off thoroughly.

[0084]

** : The magic marker back remains.

x: A magic marker cannot be wiped off.

(4) Dirt was wiped off with the dry waste cloth after the six-month direct weathering test tried with the 2 above (2) of decontamination ***** and visual observation of the remaining condition of dirt was carried out. A result is based on the following three-stage evaluation.

[0085]

O : dirt can be wiped off thoroughly.

** : Dirt remains a little.

x: Dirt cannot be wiped off.

(5) The accelerated weathering test was done with the weathering evaluation sunshine weatherometer for 2000 hours, and visual observation of the state of a coat was carried out. A result is based on the following three-stage evaluation.

[0086]

O : abnormalities are not observed in a coat at all.

** : Gloss retention decreases a little and a crack arises at the end of a base material.

x: A crack and separation arise in the whole base material.

(6) The hardness of the paint film surface was measured by the pencil scratch test of pencil hardness test JIS-K5400 of a paint film surface.

- The coated plate was produced by the same method as Embodiment 1 except having produced top coat by the combination shown in Table 2, without adding a comparative example 1- (C_0) ingredient. Then, aforementioned (1) - (6) was evaluated.

[0087]- By the same method as Embodiment 1, the coated plate was produced except having used the

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commercial fluoride paint (the new gar by TOHPE CORP. helmet **2000: white) as comparative example 2-top coat. Then, aforementioned (1) - (6) was evaluated.

- Aforementioned (1) - (6) was evaluated, using the slate plate (said base material-3) which applied comparative example 3-water glass as it is.

[0088]- By the same method as Embodiment 1, the coated plate was produced except having used the commercial acrylic resin sealer for mortar as a comparative example 4-primer paint. Then, aforementioned (1) - (6) was evaluated.

[0089]

[Table 1]

基材	実施例 1	実施例 2	実施例 3	実施例 4	実施例 5	実施例 6
プライマー塗料	基材-1 カキ -1	基材-2 カキ -2	基材-3 カキ -3	基材-4 カキ -4	基材-5 カキ -5	基材-6 カキ -6
A ₀ 成分	50	50	50	50	50	50
A ₀ -1	—	—	—	—	—	80
A ₀ -2	—	—	—	—	—	—
A ₀ -3	—	—	—	—	—	—
B ₀ -1	50	50	50	50	50	—
B ₀ -2	—	—	—	—	—	20
B ₀ -3	—	—	—	—	—	—
W ₀ =800	—	—	—	—	—	—
W ₀ =3000	5	5	5	5	5	—
W ₀ =10000	—	—	—	—	—	0.1
D ₀ 成分	2	2	2	2	2	0.5
U ₀ -β-γ- スルホン酸系樹脂 系樹脂	—	—	—	—	—	—
U ₀ -β-γ- スルホン酸系樹脂 系樹脂	—	—	—	—	—	—
(1) 耐熱性材料その1	○	○	○	○	○	○
(2) 耐熱性材料その2	5.3	6.0	5.6	5.1	6.3	4.2
(3) 耐熱性材料その1	○	○	○	○	○	○
(4) 耐熱性材料その2	○	○	○	○	○	○
(5) 耐熱性材料	○	○	○	○	○	○
(6) 耐熱性材料	4H	4H	4H	4H	4H	5H

[0090]

[Table 2]

commercial fluoride paint (the new gar by TOHPE CORP. helmet **2000: white) as comparative example 2-top coat. Then, aforementioned (1) - (6) was evaluated.

- Aforementioned (1) - (6) was evaluated, using the slate plate (said base material-3) which applied comparative example 3-water glass as it is.

[0088]- By the same method as Embodiment 1, the coated plate was produced except having used the commercial acrylic resin sealer for mortar as a comparative example 4-primer paint. Then, aforementioned (1) - (6) was evaluated.

基材	実施例 7	実施例 8	実施例 9	実施例 10	実施例 11	実施例 12
プライマー塗料	基材-1 カキ -1	基材-1 カキ -1	基材-1 カキ -1	基材-1 カキ -1	基材-1 カキ -1	基材-1 カキ -1
A ₀ 成分	—	—	—	—	—	—
A ₀ -1	—	—	—	—	—	—
A ₀ -2	—	—	—	—	—	—
A ₀ -3	50	—	—	—	—	—
B ₀ -1	—	—	—	—	—	—
B ₀ -2	—	—	—	—	—	—
B ₀ -3	40	—	—	—	—	—
W ₀ =800	30	15	—	—	—	—
W ₀ =3000	—	3	—	—	—	—
W ₀ =10000	—	2	—	—	—	—
D ₀ 成分	—	—	—	—	—	—
U ₀ -β-γ- スルホン酸系樹脂 系樹脂	—	—	—	—	—	—
U ₀ -β-γ- スルホン酸系樹脂 系樹脂	—	—	—	—	—	—
(1) 耐熱性材料その1	○	○	○	○	○	○
(2) 耐熱性材料その2	4.6	3.7	8.8	10.9	20.5	10.0
(3) 耐熱性材料その1	○	○	○	○	○	○
(4) 耐熱性材料その2	○	○	○	○	○	○
(5) 耐熱性材料	○	○	○	○	○	○
(6) 耐熱性材料	5H	5H	6H	2H	9H	4H

[0091]The coated plate of the embodiment is excellent in resistance to contamination and decontamination nature compared with the coated plate of a comparative example so that it may see to Tables 1 and 2.

[0092]

[Effect of the Invention]It excels in resistance to contamination, and can produce easily by coating work, and the coated plate concerning this invention can be attached to various parts by simple construction. After construction can maintain the resistance to contamination and endurance over the long period of time of an article to be constructed.

[0093]Since the coated plate concerning this invention is excellent also in weatherability, decontamination nature, and a mold-release characteristic, it can protect an article to be constructed from dust, dust, exhaust gas, scribble, and a poster over a long period of time, and it not only excels in resistance to contamination, but it becomes easy [washing after becoming dirty].

[Translation done.]

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1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.*** shows the word which can not be translated.

3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1]The sectional side elevation showing one embodiment of the contamination-resistant coated plate concerning this invention.

[Explanations of letters or numerals]

1 Base material

2 Primer layer

3 Finishing coat

[Translation done.]